(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平11－145107

(43)公開日　平成11年(1999)５月28日

(51)Int.Cl.[6]	識別記号	ＦＩ	
Ｈ０１Ｌ　21/306		Ｈ０１Ｌ　21/306	Ｂ

審査請求　未請求　請求項の数３　ＦＤ　（全　６　頁）

(21)出願番号　特願平9－322477

(22)出願日　平成９年(1997)11月７日

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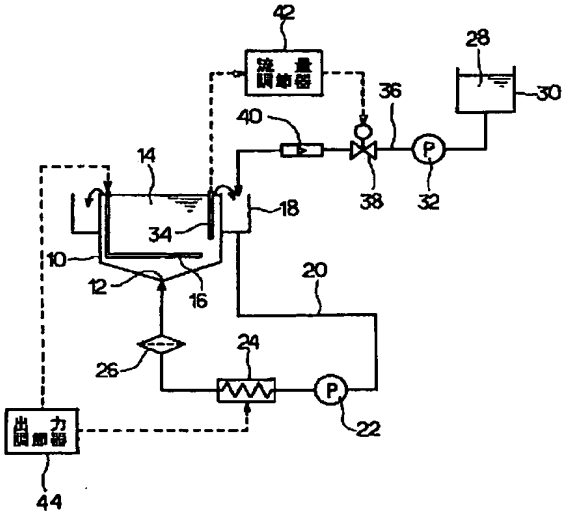
(54)【発明の名称】　基板の表面処理方法

(57)【要約】

【課題】　酸の水溶液からなる処理液を所定温度に保持しかつ所定の酸濃度に保持して常に沸騰状態に保ちながら、基板の表面上に形成された所定の被膜を選択的にエッチングできる方法を提供する。

【解決手段】　一定出力のヒータ１６、２４により処理槽１０内の処理液１４を加熱して常に沸騰状態に保つとともに、温度検出器３４によって処理液の温度を検出し、その検出温度に基づいて調節器４２により、処理液の温度が所定温度に保持されるように純水槽３０から処理液へ補充される純水２８の量を制御する。



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【特許請求の範囲】

【請求項１】　酸の水溶液からなる処理液をヒータで加熱して処理液を沸騰状態に保ち、沸騰状態の処理液中に基板を浸漬させて、基板の表面上に形成された２種類もしくはそれ以上の種類の被膜のうちの所定の被膜を選択的にエッチングする基板の表面処理方法において、

前記ヒータの出力を一定にして処理液に対し一定の熱量を与えて処理液を常に沸騰状態に保つとともに、処理液の温度を検出し、その検出温度に基づいて処理液の温度が所定温度に保持されるように処理液への純水の補充量を制御することを特徴とする基板の表面処理方法。

【請求項２】　処理液中への基板の投入時点から所定時間内だけ、および、処理液の補充時点から所定時間内だけ、それぞれヒータの出力が最大にされる請求項１記載の基板の表面処理方法。

【請求項３】　処理液が燐酸水溶液であり、基板の表面上に形成された被膜がシリコン酸化膜とシリコン窒化膜とであって、シリコン窒化膜が選択的にエッチングされる請求項１または請求項２記載の基板の表面処理方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】この発明は、半導体ウエハ、液晶表示装置用ガラス基板、電子部品などの基板を燐酸水溶液等の酸の水溶液からなる処理液中に浸漬させて表面処理する方法、特に、沸騰状態に保たれた処理液中に基板を浸漬させて、基板の表面上に形成された２種類もしくはそれ以上の種類の被膜のうちの所定の被膜を選択的にエッチングする基板の表面処理方法に関する。

【０００２】

【従来の技術】基板、例えば半導体ウエハを酸の水溶液からなる処理液、例えば燐酸水溶液中に浸漬させて、半導体ウエハの表面上に形成された２種類もしくはそれ以上の種類の被膜のうちの所定の被膜、例えばシリコン酸化膜（SiO_2膜）とシリコン窒化膜（Si_3N_4）とのうちのシリコン窒化膜を選択的にエッチングする場合には、従来、図３に概略構成を模式図で示すような表面処理装置が使用されている。この装置は、底部に液導入口１２が形設され内部に燐酸水溶液１４が貯留される処理槽１０を有し、処理槽１０の内部には、投込みヒータ１６が配設されている。そして、処理しようとする半導体ウエハは、ウエハホルダ（図示せず）に複数枚収納されて、処理槽１０内へ投入され燐酸水溶液１４中に浸漬させられる。

【０００３】処理槽１０には、溢流液受け部１８が付設されており、処理槽１０の上部から溢れ出た燐酸水溶液が溢流液受け部１８内へ流入するようになっている。溢流液受け部１８の内底部には、液循環用配管２０が連通しており、液循環用配管２０の先端は、処理槽１０の液導入口１２に連通接続されている。液循環用配管２０には、循環ポンプ２２、インラインヒータ２４およびフィルタ２６が介設されており、燐酸水溶液は、処理槽１０、溢流液受け部１８および液循環用配管２０により構成された循環経路を循環させられる。溢流液受け部１８には、純水２８が貯留された純水槽３０の内底部に一端が連通し定量ポンプ３２が介設された純水供給管５０の他端吐出口が配置されている。また、処理槽１０の内部には、温度検出器３４が配置されており、温度検出器３４は温度調節器５２に接続され、温度調節器５２は投込みヒータ１６に接続されている。さらに、液循環用配管２０の途中に温度検出器５４が介挿され、温度検出器５４は温度調節器５６に接続され、温度調節器５６はインラインヒータ２４に接続されている。

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【０００４】図３に示した構成の装置により半導体ウエハを表面処理する場合、燐酸水溶液１４は、投込みヒータ１６およびインラインヒータ２４によって１５０℃～１８０℃程度の温度に加熱される。このため、処理槽１０内の燐酸水溶液１４から水分が蒸発し、燐酸水溶液１４の燐酸濃度が上昇する。そこで、定量ポンプ３２によって純水槽３０内から純水２８を、純水供給管５０を通して供給し、純水供給管５０の吐出口から、溢流液受け部１８内に流入した燐酸水溶液に純水を連続して滴下させるようにしている。この際、従来は、純水供給管５０内を通って一定流量の純水を流し、処理槽１０内の燐酸水溶液１４から蒸発した水分量にほぼ相当する量の純水を常時補充するようにしている。また、処理槽１０内の燐酸水溶液１４の温度は、各温度検出器３４、５４から送られる検出信号に基づいて各温度調節器５２、５６により投込みヒータ１６およびインラインヒータ２４をそれぞれ制御、通常はＰＩＤ制御して、所定温度に保たれるように調節されている。

【０００５】ところで、シリコン酸化膜に対してシリコン窒化膜を選択的にエッチングする場合には、シリコン酸化膜のエッチングレートに対するシリコン窒化膜のエッチングレートの比、すなわち選択比が問題となる。また、シリコン酸化膜やシリコン窒化膜のエッチングレートは、燐酸水溶液の温度によって変化し、燐酸水溶液の温度が高くなるほど大きくなる。そして、燐酸水溶液の或る温度における選択比は、当該温度において燐酸水溶液が沸騰状態にあるとき、言い換えると、当該温度が燐酸水溶液の沸点となるような燐酸濃度であるときに、最も大きくなる。したがって、シリコン窒化膜のエッチングレートや選択比、燐酸水溶液の濃度などとの関係で適宜選定された処理温度に処理槽１０内の燐酸水溶液１４の温度を保持し、かつ、その温度において常に燐酸水溶液が沸騰している状態に保たれるように、すなわち、当該温度が燐酸水溶液の沸点となるような燐酸濃度に保たれるようにして、半導体ウエハの表面処理を行うことが重要である。

【０００６】

【発明が解決しようとする課題】処理槽１０内の燐酸水

溶液１４は、投込みヒータ１６およびインラインヒータ２４で加熱されることにより水分が蒸発して、燐酸濃度が上昇し、一方、上昇した燐酸濃度を下げるために、燐酸水溶液の循環経路中において純水槽３０から純水供給管５０を通って純水が燐酸水溶液へ補充される。したがって、燐酸水溶液１４の燐酸濃度は、燐酸水溶液１４からの水分の蒸発量と純水の補充量とによって決まり、水分蒸発量と純水補充量とが常に等しくなれば、燐酸水溶液の燐酸濃度は、一定に保たれることになる。

【０００７】一方、燐酸水溶液への純水の補充によって燐酸水溶液の熱量を奪うため、燐酸水溶液の温度が低下する。燐酸水溶液の温度が低下すると、温度検出器３４、５４からの検出信号に基づいて温度調節器５２、５６によりヒータ１６、２４が制御されて、純水の補充によって燐酸水溶液から奪われた熱量に見合った熱量が燐酸水溶液に与えられ、処理槽１０内の燐酸水溶液１４の温度が所定温度に保持される。

【０００８】ところが、従来のように燐酸水溶液へ一定量の純水を連続して補充する方法では、処理槽１０内の燐酸水溶液１４からの水分蒸発量と純水補充量とが等しくなるとは限らない。このため、処理槽１０内の燐酸水溶液１４の温度が所定温度に保持されても、その温度が燐酸水溶液の沸点となるとは限らない。このように、従来の方法では、所定温度において常に燐酸水溶液が沸騰状態に保たれるように燐酸水溶液の燐酸濃度を制御しながら、半導体ウエハの表面処理を行うことは困難であった。

【０００９】この発明は、以上のような事情に鑑みてなされたものであり、酸の水溶液からなる処理液を所定温度に保持しかつ常に沸騰状態に保ちながら、基板の表面上に形成された２種類もしくはそれ以上の種類の被膜のうちの所定の被膜を選択的にエッチングすることができる基板の表面処理方法を提供することを目的とする。

【００１０】

【課題を解決するための手段】請求項１に係る発明は、酸の水溶液からなる処理液をヒータで加熱して処理液を沸騰状態に保ち、沸騰状態の処理液中に基板を浸漬させて、基板の表面上に形成された２種類もしくはそれ以上の種類の被膜のうちの所定の被膜を選択的にエッチングする基板の表面処理方法において、前記ヒータの出力を一定にして処理液に対し一定の熱量を与えて処理液を常に沸騰状態に保つとともに、処理液の温度を検出し、その検出温度に基づいて処理液の温度が所定温度に保持されるように処理液への純水の補充量を制御することを特徴とする。

【００１１】請求項２に係る発明は、請求項１記載の方法において、処理液中への基板の投入時点から所定時間内だけ、および、処理液の補充時点から所定時間内だけ、それぞれヒータの出力を最大にすることを特徴とする。

【００１２】請求項３に係る発明は、請求項１または請求項２記載の方法において、処理液が燐酸水溶液であり、基板の表面上に形成された被膜がシリコン酸化膜とシリコン窒化膜とであって、シリコン窒化膜を選択的にエッチングすることを特徴とする。

【００１３】請求項１に係る発明の基板の表面処理方法によると、一定出力のヒータにより処理液に対し一定の熱量が与えられて、処理液が常に沸騰状態に保たれる。すなわち、処理液がヒータによって加熱されることにより、処理液から水分が蒸発して、処理液の酸濃度が上昇し、それに伴って処理液の沸点も上昇するが、処理液は、上昇した沸点まで処理液の温度を同時的に上昇させることができる程度の一定出力のヒータにより加熱されて、常に沸騰状態に保たれる。一方、処理液の温度が検出され、その検出温度に基づいて処理液の温度が所定温度に保持されるように処理液へ純水が補充される。すなわち、上記したように処理液からの水分の蒸発に伴う処理液の酸濃度の上昇（沸点の上昇）により処理液の温度が上昇するので、処理液からの水分蒸発に相応する処理液の温度上昇を検出して、その温度上昇分に対応する量の純水を処理液へ補充することにより、処理液の温度が降下して元の所定温度に保持される。この時も、処理液は沸騰状態に保たれているので、所定温度が処理液の沸点であり、処理液は、所定温度が沸点となるような元の酸濃度に保持されることとなる。このようにして、処理液は、所定温度に保持されかつ所定濃度に保持されて常に沸騰状態に保たれる。

【００１４】請求項２に係る発明の方法では、処理液中へ基板を投入した時や処理液を補充した時のように処理液の温度が瞬時に大きく低下した時に、その時点から所定時間内だけヒータの出力が最大にされるので、処理液の温度が速やかに回復する。このため、基板の表面上に形成された被膜のエッチングレートが低下するのを避けることができる。

【００１５】請求項３に係る発明の方法では、燐酸水溶液が所定温度に保持されかつ所定の燐酸濃度に保持されて常に沸騰状態に保たれ、シリコン酸化膜に対するシリコン窒化膜の選択比が大きくなった状態で、基板の表面上に形成されたシリコン窒化膜が選択的にエッチングされる。

【００１６】

【発明の実施の形態】以下、この発明の好適な実施形態について図１および図２を参照しながら説明する。

【００１７】図１は、この発明に係る基板の表面処理方法を実施するのに使用される表面処理装置の概略構成の１例を示す模式図である。図１において、図３で使用した符号と同一符号を付した構成要素は、図３に示した従来の装置と共通するものであり、それらの説明を省略する。

【００１８】この装置では、純水２８が貯留された純水

槽３０の内底部に一端が連通し他端吐出口が溢流液受け部１８に配置され定量ポンプ３２が介設された純水供給管３６に、流量制御弁３８および流量計４０が介挿されている。また、処理槽１０の内部に配置された温度検出器３４が流量調節器４２に接続され、流量調節器４２が流量制御弁３８に接続されている。さらに、投込みヒータ１６およびインラインヒータ２４に出力調節器４４が接続されている。これら以外の構成は、図３に示した従来の装置と同様である。

【００１９】図１に示した構成の装置より基板を表面処理するには、例えば表面上にシリコン酸化膜とシリコン窒化膜とが形成された半導体ウエハを燐酸水溶液によって選択的エッチングするには、出力調節器４４により投込みヒータ１６およびインラインヒータ２４の出力が常に一定となるように調節して、投込みヒータ１６およびインラインヒータ２４によって処理槽１０内の燐酸水溶液１４が１５０℃～１８０℃の所定温度に加熱されるようにする。この際のヒータ１６、２４の出力は、燐酸水溶液１４を常に沸騰状態に保つために必要な熱量が燐酸水溶液に対して与えられる程度に設定される。すなわち、燐酸水溶液から水分が蒸発して燐酸濃度が上昇し、それに伴って燐酸水溶液の沸点が上昇しても、その上昇した沸点まで燐酸水溶液の温度を同時的に上昇させることができる程度に、ヒータ１６、２４の出力が設定される。また、処理槽１０内の燐酸水溶液１４の温度が温度検出器３４によって検出され、その検出信号が流量調節器４２へ送られ、検出信号に基づいて流量調節器４２により流量制御弁３８が制御、例えばＰＩＤ制御されるようにする。そして、処理槽１０内の燐酸水溶液１４の温度が所定温度に保持されるように、純水槽３０から純水供給管３６を通って溢流液受け部１８内へ供給される純水の流量が調節され、循環経路内を循環している燐酸水溶液への単位時間当りの純水の補充量が調節される。

【００２０】上記したように、出力調節器４４により投込みヒータ１６およびインラインヒータ２４の出力を一定にするとともに、温度検出器３４によって処理槽１０内の燐酸水溶液１４の温度を検出し、流量調節器４２により流量制御弁３８を制御して、燐酸水溶液１４の温度が所定温度に保持されるように単位時間当りの純水の補充量を調節することにより、燐酸水溶液１４の燐酸濃度が一定に保持されて、燐酸水溶液１４が常に沸騰状態に保たれることとなる。すなわち、処理槽１０内の燐酸水溶液１４から水分が蒸発することにより、燐酸水溶液１４の燐酸濃度が上昇して燐酸水溶液１４の沸点が上昇し、それに伴って燐酸水溶液１４の温度が上昇するので、燐酸水溶液１４からの水分蒸発に相応する燐酸水溶液１４の温度上昇を温度検出器３４により検出して、その温度上昇分に対応する量の純水を燐酸水溶液へ補充すると、燐酸水溶液１４の温度が降下して元の所定温度に保持される。この時も、燐酸水溶液１４は沸騰状態に保

たれているので、所定温度が燐酸水溶液１４の沸点であり、燐酸水溶液１４は、所定温度が沸点となるような元の燐酸濃度に保持されることとなる。

【００２１】なお、処理槽１０内の燐酸水溶液１４中へ半導体ウエハを投入した時や処理槽１０内へ燐酸水溶液を補充した時などのように、外乱によって燐酸水溶液１４の温度が瞬時に大きく低下すると、シリコン窒化膜のエッチングレートの低下を招くこととなる。このため、処理槽１０内の燐酸水溶液１４中へのウエハの投入や処理槽１０内への燐酸水溶液の補充などによって燐酸水溶液１４の温度が瞬時に低下した時には、出力調節器４４によりヒータ１６、２４の出力を最大値に調節して燐酸水溶液１４を加熱するようにするとよい。このようにすると、燐酸水溶液１４の温度が瞬時に低下しても、燐酸水溶液１４の温度は速やかに回復するので、シリコン窒化膜のエッチングレートの低下を避けることができる。

【００２２】図２に、処理槽１０内の燐酸水溶液１４の温度変化の状態の１例を示す。まず、処理を開始して燐酸水溶液１４の温度が設定温度に到達するまでの期間Ｔ１は、出力調節器４４によりヒータ１６、２４の出力を最大値に調節して燐酸水溶液１４を加熱する。そして、燐酸水溶液１４の温度が設定温度に到達した後、処理槽１０内の燐酸水溶液１４中へウエハを投入したりあるいは処理槽１０内へ燐酸水溶液を補充したりする時点ｔまでの期間Ｔ２は、出力調節器４４によりヒータ１６、２４の出力を設定値に調節して、燐酸水溶液１４に対し一定の熱量を与え続ける。処理槽１０内の燐酸水溶液１４中へウエハを投入したりあるいは処理槽１０内へ燐酸水溶液を補充したりすると、その時点ｔから燐酸水溶液１４の温度が降下した後上昇に転じて再び設定温度に到達するまでの期間Ｔ３は、出力調節器４４によりヒータ１６、２４の出力を最大値に調節して燐酸水溶液１４に大きな熱量を与える。そして、燐酸水溶液１４の温度が設定温度に到達した以後の期間Ｔ４は、出力調節器４４によりヒータ１６、２４の出力を設定値に調節して、燐酸水溶液１４に対し一定の熱量を与え続ける。

【００２３】また、処理槽１０内の燐酸水溶液１４の温度が上昇する過程で、燐酸水溶液１４の温度が比例帯Ｐ内に入ると（ａ時点）、純水の補充を開始して補充量を徐々に増加させる。この後、燐酸水溶液１４の温度がなおも上昇して比例帯Ｐ内を出ると（ｂ時点）、純水の補充量を最大にして一定に保つ。そして、燐酸水溶液１４の温度がさらに上昇してピークに達した後降下する過程で、燐酸水溶液１４の温度が比例帯Ｐ内に入ると（ｃ時点）、純水の補充量を徐々に減少させる。この後、燐酸水溶液１４の温度がなおも降下して比例帯Ｐ内を出ると（ｄ時点）、純水の補充を停止する。純水の補充を停止してからしばらくすると、燐酸水溶液１４の温度は降下から上昇に転じる。そして、燐酸水溶液１４の温度が上昇して比例帯Ｐ内に入ると（ａ時点）、再び純水の補充

を開始して補充量を徐々に増加させる。以後、このような温度変化が繰り返される。そして、この場合、処理槽１０内の燐酸水溶液１４は常に沸騰状態に保たれているので、図２に示した定常状態での燐酸水溶液１４の温度変化は、燐酸水溶液１４の沸点の変化に対応するものであり、したがって、図２に示した燐酸水溶液１４の温度変化は、燐酸水溶液１４の燐酸濃度の変化を示していることになる。すなわち、純水の補充によって燐酸水溶液１４の燐酸濃度が低下（燐酸水溶液１４の沸点が降下）すると、それに伴って処理槽１０内の燐酸水溶液１４の温度が降下し、純水の補充を停止することによって燐酸水溶液１４からの水分蒸発により燐酸水溶液１４の燐酸濃度が上昇（燐酸水溶液１４の沸点が上昇）すると、それに伴って処理槽１０内の燐酸水溶液１４の温度が上昇することになるからである。

【００２４】なお、上記した実施形態では、温度検出器３４によって検出された燐酸水溶液１４の温度に基づいて流量調節器４２により流量制御弁３８を制御して、純水槽３０から純水供給管３６を通って溢流液受け部１８内へ供給される純水の流量を調節するようにしているが、流量制御弁３８に代えて開閉制御弁を使用して、調節器によって単位時間内に開閉制御弁を開く時間（単位時間内における純水の補充時間）を調節することにより、燐酸水溶液への単位時間当りの純水の補充量を調節するようにしてもよい。

【００２５】

【発明の効果】請求項１に係る発明の基板の表面処理方法によると、酸の水溶液からなる処理液を所定温度に保持しかつ所定の酸濃度に保持して常に沸騰状態に保ちながら、基板の表面処理を行うことができ、このため、基板の表面上に形成された２種類もしくはそれ以上の種類の被膜のうちの所定の被膜を大きな選択比でもって選択的にエッチングすることができる。

【００２６】請求項２に係る発明の方法では、処理液中へ基板を投入した時や処理液を補充した時のように処理液の温度が瞬時に大きく低下した時に、処理液の温度を＊速やかに回復させることができるので、基板の表面上に形成された被膜のエッチングレートの低下を防ぐことができる。

【００２７】請求項３に係る発明の方法では、シリコン酸化膜に対するシリコン窒化膜の選択比を大きくして、基板の表面上に形成されたシリコン窒化膜を選択的にエッチングすることができる。

【図面の簡単な説明】

【図１】この発明に係る基板の表面処理方法を実施するのに使用される表面処理装置の概略構成の１例を示す模式図である。

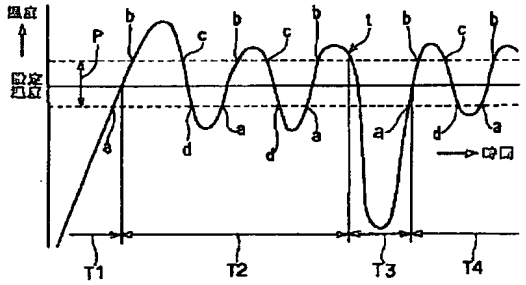
【図２】この発明に係る基板の表面処理方法を実施したときの、処理槽内の燐酸水溶液の温度変化の状態の１例を示す図である。

【図３】従来の表面処理装置の概略構成の１例を示す模式図である。

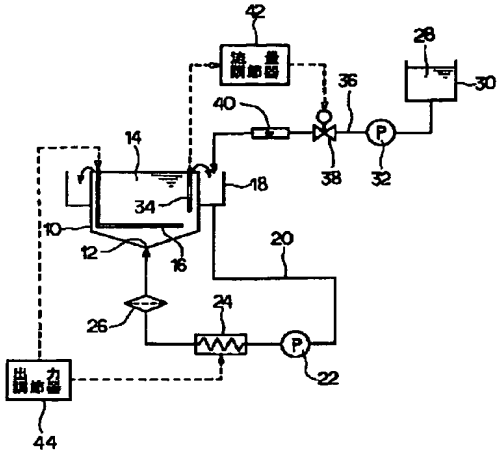
【符号の説明】

１０　処理槽
１２　処理槽底部の液導入口
１４　燐酸水溶液
１６　投込みヒータ
１８　溢流液受け部
２０　液循環用配管
２２　循環ポンプ
２４　インラインヒータ
２６　フィルタ
２８　純水
３０　純水槽
３２　定量ポンプ
３４　温度検出器
３６　純水供給管
３８　流量制御弁
４０　流量計
４２　流量調節器
４４　出力調節器

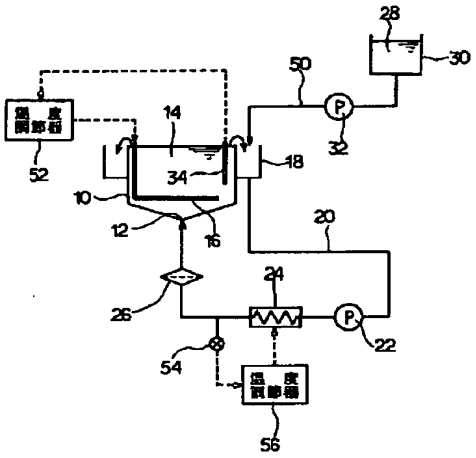
【図２】



【図１】


42
温度調節器
28
30
36
40
38
32
14
18
34
10
12
16
20
26
24
22
出力調節器
44

【図３】


28
30
50
32
温度調節器
52
14
34
18
10
12
16
20
26
24
22
54
温度調節器
56

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-145107
(43)Date of publication of application : 28.05.1999

(51)Int.Cl. H01L 21/306

(21)Application number : 09-322477
(22)Date of filing : 07.11.1997

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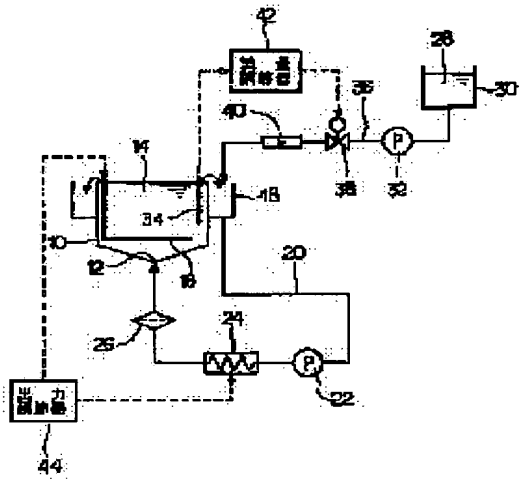
(54) SURFACE TREATMENT METHOD FOR SUBSTRATE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method which enables selective etching of a predetermined film formed on the surface of a substrate, while maintaining a treatment solution made of an acid solution constantly in a boiling state by holding the treatment solution at a predetermined temperature and a predetermined acid concentration.
SOLUTION: A treatment solution 14 in a treatment tub 10 is heated and constantly held in a boiling state by a constant-output heater 16 and 24, and the temperature of the treatment solution is detected by a temperature detector 34. On the basis of the detected temperature, the quantity of pure water 28 supplied from a pure water tub 30 to the treatment solution is controlled by a regulator 42, so that the treatment solution is held at a predetermined temperature.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] Heat at a heater processing liquid which consists of an aqueous solution of an acid, and processing liquid is maintained at an ebullition condition. In a surface treatment method of a substrate which etches selectively a predetermined coat of the coats of two kinds which a substrate was made immersed into processing liquid of an ebullition condition, and were formed on a front face of a substrate, or a class beyond it While fixing an output of said heater, giving fixed quantity of heat to processing liquid and always maintaining processing liquid at an ebullition condition A surface treatment method of a substrate characterized by controlling the amount of supplements of pure water to processing liquid so that temperature of processing liquid is detected and temperature of processing liquid is held at predetermined temperature based on the detection temperature.
[Claim 2] A surface treatment method of a substrate according to claim 1 that an output of a heater is made into max only for a processing liquid supplement-event to the inside [a substrate to inside of processing liquid charge-event to] of predetermined time and predetermined time, respectively.
[Claim 3] A surface treatment method of a substrate according to claim 1 or 2 that processing liquid is a phosphoric acid aqueous solution, a coat formed on a front face of a substrate is with silicon oxide and a silicon nitride, and a silicon nitride is etched selectively.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention makes a substrate immersed into the method of making substrates, such as a semiconductor wafer, a glass substrate for liquid crystal displays, and electronic parts, immersed into the processing liquid which consists of an aqueous solution of acids, such as a phosphoric-acid aqueous solution, and carrying out surface treatment, and the processing liquid especially maintained at the ebullition condition, and relates to the surface-treatment method of the substrate which etches selectively the predetermined coat of the coats of two kinds formed on the front face of a substrate, or the class beyond it.
[0002]
[Description of the Prior Art] A substrate, for example, a semiconductor wafer, is made immersed into the processing liquid which consists of an aqueous solution of an acid, for example, a phosphoric acid aqueous solution. The predetermined coat of the coats of two kinds formed on the front face of a semiconductor wafer, or the class beyond it, For example, when etching selectively the silicon nitride of silicon oxide (SiO_2 film) and the silicon nitrides (Si_3N_4), surface treatment equipment as shows an outline configuration to drawing 3 by the mimetic diagram is used conventionally. This equipment has the processing tub 10 in which the liquid inlet 12 is made by the pars basilaris ossis occipitalis, and the phosphoric acid aqueous solution 14 is stored inside, and the immersion heater 16 is arranged in the interior of the processing tub 10. And two or more semiconductor wafers which it is going to process are contained by the wafer holder (not shown), are thrown in into the processing tub 10, and are made to be immersed in the phosphoric acid aqueous solution 14.
[0003] The overflow liquid receptacle section 18 is attached to the processing tub 10, and the phosphoric acid aqueous solution which overflowed from the upper part of the processing tub 10 flows into the overflow liquid receptacle section 18. At the inner pars basilaris ossis occipitalis of the overflow liquid receptacle section 18, the piping 20 for liquid circulation is open for free passage, and free passage connection of the head of the piping 20 for liquid circulation is made in the liquid inlet 12 of the processing tub 10. The circulating pump 22, the in-line heater 24, and the filter 26 are interposed in the piping 20 for liquid circulation, and the circulation path constituted by the processing tub 10, the overflow liquid receptacle section 18, and the piping 20 for liquid circulation is circulated for a phosphoric acid aqueous solution. The other end delivery of the pure water supply pipe 50 with which the end was open for free passage at the inner pars basilaris ossis occipitalis of the pure water tub 30 in which pure water 28 was stored with the supply pipe, and the metering pump 32 was interposed in it is arranged at the overflow liquid receptacle section 18. Moreover, the thermometric element 34 is arranged inside the processing tub 10, a thermometric element 34 is connected to a thermoregulator 52, and the thermoregulator 52 is connected to the immersion heater 16. Furthermore, a thermometric element 54 is inserted in the middle of the piping 20 for liquid circulation, a thermometric element 54 is connected to a thermoregulator 56, and the thermoregulator 56 is connected to the in-line heater 24.
[0004] When carrying out surface treatment of the semiconductor wafer with the equipment of a

configuration of having been shown in drawing 3 , the phosphoric acid aqueous solution 14 is heated by the temperature of 150 degrees C – about 180 degrees C at an immersion heater 16 and the in-line heater 24. For this reason, moisture evaporates from the phosphoric acid aqueous solution 14 in the processing tub 10, and the phosphoric acid concentration of the phosphoric acid aqueous solution 14 rises. Then, pure water 28 is supplied through the pure water supply pipe 50 from the inside of the pure water tub 30, and he follows the phosphoric acid aqueous solution which flowed in the overflow liquid receptacle section 18, and is trying to make pure water dropped at it from the delivery of the pure water supply pipe 50 with a metering pump 32. Under the present circumstances, he is trying to always fill up conventionally the pure water of the amount which is mostly equivalent to the moisture content which evaporated the pure water of constant flow through the inside of the pure water supply pipe 50 from the sink and the phosphoric acid aqueous solution 14 in the processing tub 10. Moreover, based on the detecting signal to which the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 is sent from each thermometric elements 34 and 54, control and usual carry out PID control of an immersion heater 16 and the in-line heater 24 with each thermoregulators 52 and 56, respectively, and it is adjusted so that it may be maintained at predetermined temperature.
[0005] By the way, in etching a silicon nitride selectively to silicon oxide, the ratio of the etching rate of the silicon nitride to the etching rate of silicon oxide, i.e., a selection ratio, poses a problem. Moreover, the etching rate of silicon oxide or a silicon nitride changes with the temperature of a phosphoric acid aqueous solution, and becomes so large that the temperature of a phosphoric acid aqueous solution becomes high. And when a phosphoric acid aqueous solution is in an ebullition condition in the temperature concerned, the selection ratio in a certain temperature of a phosphoric acid aqueous solution is put in another way and it is the phosphoric acid concentration from which the temperature concerned serves as the boiling point of a phosphoric acid aqueous solution, it becomes the largest. Therefore, it is important to perform surface treatment of a semiconductor wafer, as it is maintained at phosphoric acid concentration from which the temperature concerned serves as the boiling point of a phosphoric acid aqueous solution so that it may be maintained at the condition that held the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 to the processing temperature suitably selected by the relation between the etching rate of a silicon nitride, the concentration of a selection ratio and a phosphoric acid aqueous solution, etc., and the phosphoric acid aqueous solution has always boiled in the temperature.
[0006]
[Problem(s) to be Solved by the Invention] Moisture evaporates by heating the phosphoric acid aqueous solution 14 in the processing tub 10 at an immersion heater 16 and the in-line heater 24, phosphoric acid concentration rises, and on the other hand, in order to lower the phosphoric acid concentration which rose, a phosphoric acid aqueous solution is supplemented with pure water through the pure water supply pipe 50 from the pure water tub 30 into the circulation path of a phosphoric acid aqueous solution. Therefore, if the phosphoric acid concentration of the phosphoric acid aqueous solution 14 is decided by the evaporation of the moisture from the phosphoric acid aqueous solution 14, and the amount of supplements of pure water and moisture evaporation and the amount of pure water supplements always become equal, the phosphoric acid concentration of a phosphoric acid aqueous solution will be kept constant.
[0007] On the other hand, in order to take the quantity of heat of a phosphoric acid aqueous solution by supplement of pure water in a phosphoric acid aqueous solution, the temperature of a phosphoric acid aqueous solution falls. If the temperature of a phosphoric acid aqueous solution falls, based on the detecting signal from thermometric elements 34 and 54, heaters 16 and 24 will be controlled by thermoregulators 52 and 56, the quantity of heat corresponding to the quantity of heat taken from the phosphoric acid aqueous solution by the supplement of pure water will be given to a phosphoric acid aqueous solution, and the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 will be held at predetermined temperature.
[0008] However, by the method of supplementing a phosphoric acid aqueous solution with the pure water of a constant rate continuously like before, the moisture evaporation and the amount of pure water supplements from the phosphoric acid aqueous solution 14 in the processing tub

10 do not necessarily become equal. For this reason, even if the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 is held at predetermined temperature, that temperature does not necessarily serve as the boiling point of a phosphoric acid aqueous solution. Thus, it was difficult to perform surface treatment of a semiconductor wafer, controlling the phosphoric acid concentration of a phosphoric acid aqueous solution by the conventional method so that a phosphoric acid aqueous solution is always maintained at an ebullition condition in predetermined temperature.

[0009] This invention aims at offering the surface treatment method of the substrate which can etch selectively the predetermined coat of the coats of two kinds formed on the front face of a substrate , or the class beyond it , holding the processing liquid which is make in view of the above situations and consists of an aqueous solution of an acid to predetermined temperature , and always maintaining at an ebullition condition .

[0010]

[Means for Solving the Problem] Invention concerning claim 1 heats at a heater processing liquid which consists of an aqueous solution of an acid, and maintains processing liquid at an ebullition condition. In a surface treatment method of a substrate which etches selectively a predetermined coat of the coats of two kinds which a substrate was made immersed into processing liquid of an ebullition condition, and were formed on a front face of a substrate, or a class beyond it While fixing an output of said heater, giving fixed quantity of heat to processing liquid and always maintaining processing liquid at an ebullition condition, temperature of processing liquid is detected and it is characterized by controlling the amount of supplements of pure water to processing liquid so that temperature of processing liquid is held at predetermined temperature based on the detection temperature.

[0011] Invention concerning claim 2 is characterized by only a processing liquid supplement-event to the inside [a substrate to inside of processing liquid charge-event to] of predetermined time and predetermined time making an output of a heater max, respectively in a method according to claim 1.

[0012] In a method according to claim 1 or 2, processing liquid is a phosphoric acid aqueous solution, a coat formed on a front face of a substrate is with silicon oxide and a silicon nitride, and invention concerning claim 3 is characterized by etching a silicon nitride selectively.

[0013] According to a surface treatment method of a substrate invention concerning claim 1, fixed quantity of heat is given to processing liquid at a heater of a fixed output, and processing liquid is maintained at an ebullition condition. That is, although moisture evaporates from processing liquid, acid concentration of processing liquid rises and the boiling point of processing liquid also goes up in connection with it by heating processing liquid at a heater, processing liquid is heated at a heater of a fixed output which is the degree which can raise temperature of processing liquid on a simultaneous target till the boiling point which went up, and is always maintained at an ebullition condition. On the other hand, temperature of processing liquid is detected, and processing liquid is supplemented with pure water so that temperature of processing liquid may be held at predetermined temperature based on the detection temperature. That is, since temperature of processing liquid rises by lifting (lifting of the boiling point) of acid concentration of processing liquid accompanying evaporation of moisture from processing liquid as described above, temperature of processing liquid descends and it is held at the original predetermined temperature by detecting a temperature rise of processing liquid which ****s in moisture evaporation from processing liquid, and supplementing processing liquid with pure water of an amount corresponding to a part for the temperature rise. Since, as for processing liquid, it is maintained at an ebullition condition also at this time, predetermined temperature is the boiling point of processing liquid, and processing liquid will be held at acid concentration of origin from which predetermined temperature serves as the boiling point. Thus, processing liquid is held at predetermined temperature, and is held at predetermined concentration, and is always maintained at an ebullition condition.

[0014] When temperature of processing liquid falls greatly in an instant like [when replacing a time of throwing in a substrate into processing liquid, and processing liquid with a method of invention concerning claim 2], since an output of a heater is made into max, temperature of

processing liquid recovers only the inside of predetermined time promptly from the event. For this reason, it is avoidable that an etching rate of a coat formed on a front face of a substrate falls.
[0015] By method of invention concerning claim 3, a phosphoric acid aqueous solution is held at predetermined temperature, and it is held at predetermined phosphoric acid concentration, and is always maintained at an ebullition condition, and after a selection ratio of a silicon nitride to silicon oxide has become large, a silicon nitride formed on a front face of a substrate is etched selectively.
[0016]
[Embodiment of the Invention] It explains referring to drawing 1 and drawing 2 about the suitable operation gestalt of this invention hereafter.
[0017] Drawing 1 is the mimetic diagram showing one example of the outline configuration of the surface treatment equipment used for enforcing the surface treatment method of the substrate concerning this invention. In drawing 1 , the component which attached the same sign as the sign used by drawing 3 is common to the conventional equipment shown in drawing 3 , and omits those explanation.
[0018] With this equipment, the flow control valve 38 and the flowmeter 40 are inserted in the pure water supply pipe 36 with which the end was open for free passage with the supply pipe at the inner pars basilaris ossis occipitalis of the pure water tub 30 in which pure water 28 was stored, the other end delivery has been arranged at the overflow liquid receptacle section 18, and the metering pump 32 was interposed. Moreover, the thermometric element 34 arranged inside the processing tub 10 is connected to a flow regulator 42, and the flow regulator 42 is connected to the flow control valve 38. Furthermore, the output-control machine 44 is connected to the immersion heater 16 and the in-line heater 24. The configuration of those other than these is the same as that of the conventional equipment shown in drawing 3 .
[0019] In order to carry out surface treatment of the substrate from the equipment of a configuration of having been shown in drawing 1 (for example, for carrying out alternative etching of the semiconductor wafer with which silicon oxide and a silicon nitride were formed on the front face with a phosphoric acid aqueous solution), it adjusts so that the output of an immersion heater 16 and the in-line heater 24 may become always fixed with the output-control vessel 44, and the phosphoric acid aqueous solution 14 in the processing tub 10 is heated at an immersion heater 16 and the in-line heater 24 by the predetermined temperature which is 150 degrees C - 180 degrees C. The output of the heaters 16 and 24 in this case is set as the degree to which quantity of heat required in order to always maintain the phosphoric acid aqueous solution 14 at an ebullition condition is given to a phosphoric acid aqueous solution. That is, even if moisture evaporates from a phosphoric acid aqueous solution, phosphoric acid concentration rises and the boiling point of a phosphoric acid aqueous solution goes up in connection with it, the output of heaters 16 and 24 is set as the degree which can raise the temperature of a phosphoric acid aqueous solution on a simultaneous target till the boiling point which went up. moreover, the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 is detected by the thermometric element 34, and the detecting signal sends to a flow regulator 42 -- having -- a detecting signal -- being based -- a flow regulator 42 -- a flow control valve 38 -- control -- for example, PID control is made to be carried out. And the flow rate of the pure water supplied into the overflow liquid receptacle section 18 through the pure water supply pipe 36 from the pure water tub 30 is adjusted, and the amount of supplements of the pure water per unit time amount to the phosphoric acid aqueous solution which circulates through the inside of a circulation path is adjusted so that the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 may be held at predetermined temperature.
[0020] As described above, while fixing the output of an immersion heater 16 and the in-line heater 24 with the output-control vessel 44 A thermometric element 34 detects the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10, and a flow control valve 38 is controlled by the flow regulator 42. By adjusting the amount of supplements of the pure water per unit time amount so that the temperature of the phosphoric acid aqueous solution 14 may be held at predetermined temperature, the phosphoric acid concentration of the phosphoric acid

aqueous solution 14 will be held uniformly, and the phosphoric acid aqueous solution 14 will always be maintained at an ebullition condition. Namely, since the phosphoric acid concentration of the phosphoric acid aqueous solution 14 rises, the boiling point of the phosphoric acid aqueous solution 14 goes up and the temperature of the phosphoric acid aqueous solution 14 rises in connection with it when moisture evaporates from the phosphoric acid aqueous solution 14 in the processing tub 10 If a thermometric element 34 detects the temperature rise of the phosphoric acid aqueous solution 14 which ****s in moisture evaporation from the phosphoric acid aqueous solution 14 and a phosphoric acid aqueous solution is supplemented with the pure water of the amount corresponding to a part for the temperature rise, the temperature of the phosphoric acid aqueous solution 14 will descend, and it will be held at the original predetermined temperature. Since, as for the phosphoric acid aqueous solution 14, it is maintained at the ebullition condition also at this time, predetermined temperature is the boiling point of the phosphoric acid aqueous solution 14, and the phosphoric acid aqueous solution 14 will be held at the phosphoric acid concentration of origin from which predetermined temperature serves as the boiling point.

[0021] In addition, when a phosphoric acid aqueous solution is filled up into the time of throwing in a semiconductor wafer into the phosphoric acid aqueous solution 14 in the processing tub 10, or the processing tub 10, when the temperature of the phosphoric acid aqueous solution 14 falls greatly according to disturbance in an instant, lowering of the etching rate of a silicon nitride will be caused like. For this reason, when the temperature of the phosphoric acid aqueous solution 14 falls in an instant by the charge of the wafer to the inside of the phosphoric acid aqueous solution 14 in the processing tub 10, supplement of the phosphoric acid aqueous solution into the processing tub 10, etc., it is good to adjust the output of heaters 16 and 24 to maximum with the output-control vessel 44, and to heat the phosphoric acid aqueous solution 14. Since the temperature of the phosphoric acid aqueous solution 14 will be promptly recovered even if the temperature of the phosphoric acid aqueous solution 14 falls in an instant if it does in this way, lowering of the etching rate of a silicon nitride is avoidable.

[0022] One example of the condition of the temperature change of the phosphoric acid aqueous solution 14 in the processing tub 10 is shown in drawing 2 . First, the period T1 until it starts processing and the temperature of the phosphoric acid aqueous solution 14 reaches laying temperature adjusts the output of heaters 16 and 24 to maximum with the output-control vessel 44, and heats the phosphoric acid aqueous solution 14. And the period T2 by the event t of throwing in a wafer into the phosphoric acid aqueous solution 14 in the processing tub 10, or filling up a phosphoric acid aqueous solution into the processing tub 10, after the temperature of the phosphoric acid aqueous solution 14 reaches laying temperature adjusts the output of heaters 16 and 24 to the set point with the output-control vessel 44, and continues giving fixed quantity of heat to the phosphoric acid aqueous solution 14. If a wafer is thrown in into the phosphoric acid aqueous solution 14 in the processing tub 10 or a phosphoric acid aqueous solution is filled up into the processing tub 10, period T3 until it changes to backward lifting to which the temperature of the phosphoric acid aqueous solution 14 descended from the event t and reaches laying temperature again will adjust the output of heaters 16 and 24 to maximum with the output-control vessel 44, and will give big quantity of heat to the phosphoric acid aqueous solution 14. And period T four after the temperature of the phosphoric acid aqueous solution 14 reached laying temperature adjusts the output of heaters 16 and 24 to the set point with the output-control vessel 44, and continues giving fixed quantity of heat to the phosphoric acid aqueous solution 14.

[0023] Moreover, when the temperature of the phosphoric acid aqueous solution 14 enters in a proportional band P (at the a event), a supplement of pure water is started and the amount of supplements is made to increase gradually in the process in which the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 rises. Then, if the temperature of the phosphoric acid aqueous solution 14 rises still more and comes out of the inside of a proportional band P (at the b event), the amount of supplements of pure water will be made into max, and will be kept constant. And in the process which descends after the temperature of the phosphoric acid aqueous solution 14 rises further and reaches a peak, if the temperature of the

phosphoric acid aqueous solution 14 enters in a proportional band P (at the c event), the amount of supplements of pure water will be decreased gradually. Then, if the temperature of the phosphoric acid aqueous solution 14 descends still more and comes out of the inside of a proportional band P (at the d event), a supplement of pure water will be stopped. After stopping a supplement of pure water, the temperature of the phosphoric acid aqueous solution 14 starts to go up from a drop after a while. And when the temperature of the phosphoric acid aqueous solution 14 rises and it enters in a proportional band P (at the a event), a supplement of pure water is started again and the amount of supplements is made to increase gradually. Henceforth, such a temperature change is repeated. And since the phosphoric acid aqueous solution 14 in the processing tub 10 is always maintained at the ebullition condition in this case, the temperature change of the phosphoric acid aqueous solution 14 in the steady state shown in drawing 2 will correspond to change of the boiling point of the phosphoric acid aqueous solution 14, and the temperature change of the phosphoric acid aqueous solution 14 shown in drawing 2 will show change of the phosphoric acid concentration of the phosphoric acid aqueous solution 14. Namely, if the phosphoric acid concentration of the phosphoric acid aqueous solution 14 falls by supplement of pure water (the boiling point of the phosphoric acid aqueous solution 14 descends) If the phosphoric acid concentration of the phosphoric acid aqueous solution 14 rises by moisture evaporation from the phosphoric acid aqueous solution 14 by the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 descending in connection with it, and stopping a supplement of pure water (the boiling point of the phosphoric acid aqueous solution 14 goes up) It is because the temperature of the phosphoric acid aqueous solution 14 in the processing tub 10 will rise in connection with it.

[0024] In addition, although he is trying to adjust the flow rate of the pure water which controls a flow control valve 38 by the flow regulator 42 based on the temperature of the phosphoric acid aqueous solution 14 detected by the thermometric element 34, and is supplied into the overflow liquid receptacle section 18 through the pure water supply pipe 36 from the pure water tub 30 with the above-mentioned operation gestalt You may make it adjust the amount of supplements of the pure water per unit time amount to a phosphoric acid aqueous solution by replacing with a flow control valve 38, using a closing motion control valve, and adjusting the time amount (supplement time amount of the pure water within unit time amount) which opens a closing motion control valve in unit time amount with a controller.

[0025]

[Effect of the Invention] Surface treatment of a substrate can be performed holding the processing liquid which consists of an aqueous solution of an acid to predetermined temperature, and holding to predetermined acid concentration, and maintaining at an ebullition condition according to the surface treatment method of the substrate invention concerning claim 1. This sake, It can etch selectively that a big selection ratio is also about the predetermined coat of the coats of two kinds formed on the front face of a substrate, or the class beyond it.

[0026] Since the temperature of processing liquid can be promptly recovered when the temperature of processing liquid falls greatly in an instant like [when replacing the time of throwing in a substrate into processing liquid, and processing liquid with the method of invention concerning claim 2], lowering of the etching rate of the coat formed on the front face of a substrate can be prevented.

[0027] By the method of invention concerning claim 3, the selection ratio of the silicon nitride to silicon oxide can be enlarged, and the silicon nitride formed on the front face of a substrate can be etched selectively.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the mimetic diagram showing one example of the outline configuration of the surface treatment equipment used for enforcing the surface treatment method of the substrate concerning this invention.
[Drawing 2] It is drawing showing one example of the condition of the temperature change of the phosphoric acid aqueous solution in a processing tub when enforcing the surface treatment method of the substrate concerning this invention.
[Drawing 3] It is the mimetic diagram showing one example of the outline configuration of conventional surface treatment equipment.
[Description of Notations]
10 Processing Tub
12 Liquid Inlet of Processing Bottom of the Tank Section
14 Phosphoric Acid Aqueous Solution
16 Immersion Heater
18 Overflow Liquid Receptacle Section
20 Piping for Liquid Circulation
22 Circulating Pump
24 In-line Heater
26 Filter
28 Pure Water
30 Pure Water Tub
32 Metering Pump
34 Thermometric Element
36 Pure Water Supply Pipe
38 Flow Control Valve
40 Flowmeter
42 Flow Regulator
44 Output-Control Machine

[Translation done.]